

**WHAT IS CLAIMED IS:**

- Sub 3
1. A method of manufacture comprising:
    - (a) producing raw nanostructure or nanotube-containing material comprising closed structures;
    - (b) purifying the raw material;
    - (c) processing the purified material thereby forming openings in the closed structures;
    - (d) introducing a foreign species comprising electron donors or electron acceptors into at least some of the openings; and
    - (e) closing the openings, thereby forming capsules filled with the foreign species.
  2. The method of claim 1, wherein step (a) comprises producing single-walled carbon nanotube-containing material.
  3. The method of claim 1, wherein step (a) comprises producing multi-walled carbon nanotube-containing material.
  4. The method of claim 1, wherein step (a) comprises directionally growing carbon nanotubes on a support surface.
  5. The method of claim 1, wherein step (a) comprises producing carbon nanoparticles with concentric fullerene-type structures.
  6. The method of claim 1, wherein step (a) comprises producing nanotube structures with composition of  $B_xC_yN_z$ , where B = boron, C = carbon, and N = nitrogen.

7. The method of claim 1, wherein step (a) comprises producing nanotube structures with composition of  $MS_2$ , where M = tungsten, molybdenum or vanadium oxide.

8. The method of claim 1, wherein step (a) comprises producing concentric fullerene structures with composition of  $MS_2$ , where M = tungsten, molybdenum or vanadium oxide.

9. The method of claim 1, wherein step (b) comprises subjecting the raw material to ultrasonic filtration.

10. The method of claim 1, wherein step (b) comprises subjecting the raw material to a reflux procedure in an acidic medium.

11. The method of claim 1, wherein step (b) comprises subjecting the raw material first to a reflux procedure in an acidic medium, then to filtration.

12. The method of claim 11, wherein the acidic medium comprises peroxide in water, with a peroxide concentration of 1-40 volume %.

13. The method of claim 12, wherein 10-100 ml of peroxide is introduced into the medium for every 1-10 mg of carbon nanotubes, and the reflux reaction is carried out at a temperature of 20-100°C.

14. The method of claim 1, wherein step (b) comprises subjecting the raw material to oxidation in air or oxygen environment at a temperature of 300-600°C.

15. The method of claim 1, wherein step (c) comprises ultrasonication of the purified material in an acidic medium.

16. The method of claim 1, wherein step (c) comprises milling the purified material.

17. The method of claim 1, wherein step (c) comprises bombarding the purified material with ions, then subjecting the material to ultrasonication in an acidic medium.

18. The method of claim 1, wherein step (c) comprises subjecting the purified material to plasma etching.

19. The method of claim 18, wherein the plasma etching comprises etching with hydrogen or oxygen plasma.

20. The method of claim 1, wherein the foreign species of step (d) comprises at least one alkali metal or an alloy of an alkali metal.

21. The method of claim 20, wherein the at least one alkali metal comprises Li, Na, K, Rb or Cs.

22. The method of claim 1, wherein the foreign species of step (d) comprises at least one of Mg, Ca, Sr, Ba, or an alloy thereof.

23. The method of claim 1, wherein the foreign species of step (d) comprises at least one of Sc, Y, Fe, Co, Ni, Cu, or an alloy thereof.

24. The method of claim 1, wherein the foreign species of step (d) comprises at least one of a Lewis acid, halogen mixture, metal chloride, metal bromide, metal fluoride, metal oxyhalide, an acidic oxide, and a strong acid.

25. The method of claim 24, wherein the Lewis acid comprises halogen  $\text{Br}_2$ , the acidic oxide comprises  $\text{N}_2\text{O}_5$  or  $\text{SO}_3$ , and the strong acid comprises  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ .

26. The method of claim 1, wherein the foreign species of step (d) comprises cesium.

27. The method of claim 1, wherein step (d) comprises vapor phase transportation of the foreign species.

28. The method of claim 1, wherein step (d) comprises evaporation of the foreign species from a source.

29. The method of claim 1, wherein step (d) comprises solid state reaction of chemicals containing the foreign species and the processed purified material.

30. The method of claim 1, wherein step (d) comprises electrochemical reaction between the foreign species and the processed purified material.

31. The method of claim 1, wherein step (e) comprises forming passivation layers thereby enclosing the foreign species within the filled capsules.

32. The method of claim 31, wherein the passivation layers are formed by dispersing the filled capsules in a solvent.

33. The method of claim 31, wherein the passivation layers are formed by exposing the filled capsules to oxygen or an oxygen-containing gas.

34. The method of claim 1, further comprising:  
(f) removing reaction products from the outer surfaces of the filled capsules.

35. The method of claim 1, further comprising:  
(f) forming a field-emitting cathode by screen printing, electrophoretic deposition, spin coating, casting, spraying or sputtering of the capsules.

36. The method of claim 1, wherein the materials produced after step (d) have a chemical composition of  $A_xC$  where  $x$  equals 0 to 1, and A is the foreign species which comprises at least one of: Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, Fe, Co, Ni, Cu, or alloys thereof; a Lewis acid; halogen mixtures; metal chlorides; metal bromides; metal fluorides; metal oxyhalides; acidic oxides; and strong acids.

37. The method of claim 36, wherein the materials produced after step (e) have a chemical composition of  $A_xC$  where  $x$  equals 0 to 1, and A is the foreign species which comprises at least one of: Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, Fe, Co, Ni, Cu, or alloys thereof; a Lewis acid; halogen mixtures; metal chlorides; metal bromides; metal fluorides; metal oxyhalides; acidic oxides; and strong acids.

38. The method of claim 36, wherein the Lewis acid comprises halogen  $\text{Br}_2$ , the acidic oxide comprises  $\text{N}_2\text{O}_5$  or  $\text{SO}_3$ , and the strong acid comprises  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ .

39. The method of claim 1, wherein the materials produced after step (d) have an electronic workfunction of less than 5.5 eV.

40. The method of claim 1, wherein the materials produced after step (d) have an electronic workfunction of less than 4 eV.

41. The method of claim 1, wherein the materials produced after step (d) have an electronic workfunction of less than 3 eV.

42. The method of claim 1, wherein the materials produced after step (e) have an electronic workfunction of less than 5 eV.

43. The method of claim 1, wherein the materials produced after step (e) have an electronic workfunction of less than 4 eV.

44. The method of claim 1, wherein the materials produced after step (e) have an electronic workfunction of less than 3 eV.

45. The method of claim 1, further comprising varying the electronic workfunction of the materials produced after step (d) by 0 to 3 eV by controlling the amount of foreign species intercalated.

46. The method of claim 1, further comprising varying the electronic workfunction of the materials produced after step (e) by 0 to 3 eV by controlling the amount of foreign species intercalated.

47. The method of claim 1, wherein the materials produced after step (d) have a metallic behavior.

48. The method of claim 1, wherein the materials produced after step (e) have a metallic behavior.

49. A method of reducing electronic work function, reducing threshold field emission values, converting semiconducting behavior to metallic behavior, increasing the electron density state at the Fermi level, and increasing electron emission site density, of carbon nanotube-containing material, the method comprising:

- (a) forming openings in the carbon nanotube-containing material;
- (b) introducing a foreign species comprising an alkali metal, an alkaline earth metal, a mixture of alkali metals, a mixture of alkaline earth metals, or a mixture of alkali and alkaline earth metals, into at least some of the openings; and
- (c) closing the openings, thereby forming carbon nanotube capsules filled with the foreign species.

50. The method of claim 49, wherein step (a) comprises oxidizing the carbon nanotube-containing material in an acidic medium or milling the carbon nanotube-containing material.

51. The method of claim 50, wherein step (c) comprises forming passivation layers by dispersing the filled carbon nanotube-containing material in a solvent.

52. The method of claim 1, further comprising:

(d) forming a field-emitting flat panel display element comprising, at least in part, the capsules.

53. A method of manufacture comprising:

- (a) producing vertically oriented carbon nanotubes on a support surface;
- (b) applying an insulating layer;
- (c) opening tops of the nanotubes;
- (d) introducing a foreign species into the open tops and into interior spaces of the nanotubes;
- (e) closing the open tops of the nanotubes; and
- (f) activating the filled nanotubes.

54. The method of claim 53, wherein step (a) comprises producing the nanotubes by chemical vapor deposition.

55. The method of claim 53, wherein the insulating layer in step (b) comprises a polymer.

56. The method of claim 53, wherein step (c) comprises etching.

57. The method of claim 56, wherein step (c) comprises chemical etching, hydrogen plasma etching or oxygen plasma etching.



58. The method of claim 57, wherein step (c) includes removal of at least a portion of the insulating layer.

59. The method of claim 53, wherein step (d) comprises evaporation of the foreign species.

60. The method of claim 53, wherein step (d) comprises electrochemical reaction of the foreign species.

61. ~~The method of claim 53, wherein step (e) comprises forming passivation layers, thereby closing the open ends.~~

62. The method of claim 53, wherein step (f) comprises exposing the filled nanotubes to hydrogen plasma.

63. An electron field-emitting device comprising capsules formed by the method of claim 49.

64. ~~The device of claim 63, wherein the device comprises an x-ray tube, a gas discharge device, a lighting device, a microwave amplifier, an ion gun, or an electron beam lithography device.~~

65. An article of manufacture comprising capsules formed by the method of claim 1, the article having an electron emission turn-on field to obtain an electron emission current density of  $0.01\text{mA}/\text{cm}^2$  of less than  $2\text{V}/\mu\text{m}$ .

66. The article of claim 65, wherein the turn-on field is less than  $1\text{V}/\mu\text{m}$ .

67. The article of claim 65, wherein the turn-on field of less than 0.5 V/ $\mu$ m.

68. An article of manufacture comprising capsules formed by the method of claim 1, the article being capable of sustained electron emission at a current density over 1mA/cm<sup>2</sup>.

69. The article of claim 68, capable of sustained electron emission at a current density over 10 mA/cm<sup>2</sup>.

70. The article of claim 68, capable of sustained electron emission at a current density over 100 mA/cm<sup>2</sup>.

add B<sup>13</sup>  
add C<sup>9</sup>